

# Towards a Coupled Multiphysics Model of Molten Salt Battery Mechanics

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**Abstract:** When molten salt batteries activate, a number of mechanical processes take place over a very short time span. First, electrolyte that is originally located in the separator wicks into the porous anode and cathode materials under capillary forces, enabling the electrochemical activation of the battery. Second, typically the stack axially compresses by 10 to 20 percent due to the melting of the electrolyte and rearrangement of the solid network, also leading to additional electrolyte flow. These mechanical behaviors influence battery performance, and a number of open questions remain as to how the mechanical behavior depends on processing and operational parameters.

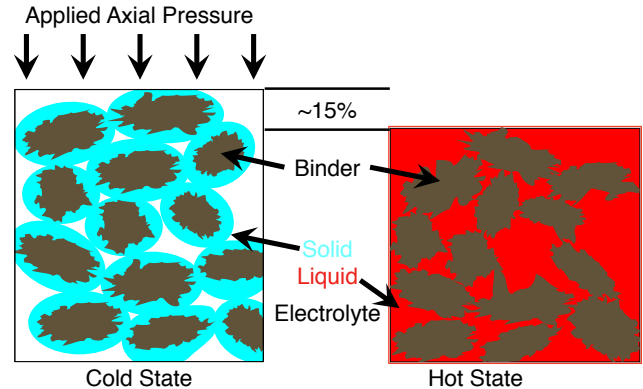
In this work, we develop a computational model based on the finite element method to study these mechanical behaviors. This model couples heat transport, two-phase porous flow, and solid deformation to study the battery activation process. We demonstrate a custom constitutive model for the solid stress, explore how it behaves with and without the presence of the liquid electrolyte, and compare simulations to experimental measurements. We also demonstrate the interplay between capillary wicking and deformation-driven flow.

**Keywords:** molten salt battery; multiphysics model; thermal transport; porous flow; mechanical deformation

## Introduction

The electrochemical cells that comprise typical molten salt batteries consist of individual layers that are manufactured by pressing the constituent materials into pellets. These pellets are stacked into a case, often including other materials such as insulation, and sealed under a significant axial closing force. When the battery is activated, the solid electrolyte that was pressed into the separator and cathode, and sometimes the anode, melts and flows throughout the battery, enabling the closure of the electrochemical circuit. The result of this electrolyte flow is a rearrangement of the granular network of the pellets, particularly the separator, that can lead to an axial compression of 10 to 20 percent. This process is illustrated schematically in Figure 1.

Details of the cell consolidation process are important to battery performance for a number of reasons. First, the detailed timing of the electrolyte melting and flow governs the cell electrochemical potential rise time behavior of the battery. Previous modeling efforts to understand rise time have only focused on the thermal problem, assuming that the battery is active as soon as any section of the separator melts. However, this approach neglects the kinetics inherent in electrolyte flow and how the properties of the porous medium evolve as a func-



**Figure 1.** Schematic of the separator pellet in the cold state (left) compared to the hot state (right), showing axial compression upon melting of the electrolyte.

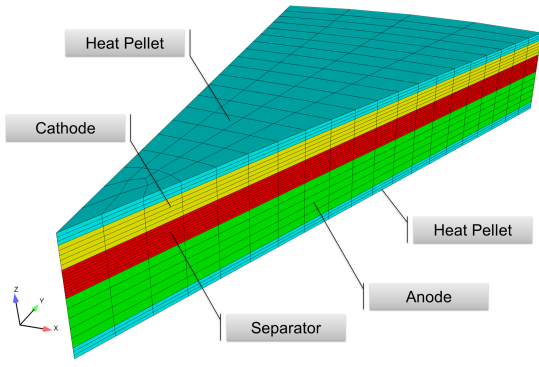
tion of temperature and the pressure distribution in the battery. Secondly, the axial deformation of the separator is critical to performance. Too much deformation can cause electrolyte to leak out of the separator, potentially causing a short circuit. Too little deformation could cause poor contact between the pellets, which inherently have non-planar surfaces, resulting in a contact resistance [1].

Historically, computer models of molten salt battery performance have focused on thermal transport (for rise time and lifetime) and the electrochemistry (for understanding voltage response and lifetime as a function of the current draw). However, in this paper we discuss the development of a multiphysics model of molten salt battery performance that includes solid deformation, electrolyte transport, and thermal transport, with future couplings to a detailed electrochemistry model. We begin by discussing models for the additional physics of solid deformation and electrolyte flow. We then discuss our vision for a fully-coupled computational simulation framework, then demonstrate some of the physics models individually.

## Model

In this paper, we discuss the development of a computational model for thermal battery performance that couples thermal transport, electrolyte transport (porous flow), solid mechanics, and electrochemistry. This model is developed within the Sierra mechanics framework [2], primarily in Sierra/Aria [3], and is based on the finite element method. All simulations are done in the three-dimensional wedge shown in Figure 2.

In the following sub-sections, we discuss the models for thermal transport, electrolyte transport, and solid mechanics.



**Figure 2.** Schematic of a generic wedge-like section of a single battery cell used for simulations. Blue is the heat pellet, yellow is the cathode, red is the separator, and green is the anode.

Since electrochemistry is only considered here in the context of a future coupling, the models for that are omitted. We conclude by discussing options for multiphysics coupling.

*Thermal transport:* For thermal transport, a standard Fourier-diffusion governing equation is used,

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot \kappa \nabla T + S_E, \quad (1)$$

where  $\rho$  is the density,  $C_p$  is the heat capacity,  $T$  is temperature,  $t$  is time,  $\kappa$  is the thermal conductivity, and  $S_E$  is a volumetric energy source. The critical energy source is from the burning of the heat pellets. This burning process is tracked using a level-set method based on a fast-marching algorithm, with the burn speed of the heat pellet specified a-priori [4].

*Fluid transport:* Transport of the molten electrolyte through the battery cell is captured using a two-phase porous flow formulation,

$$\frac{\partial(\phi \rho_a S_a)}{\partial t} = \nabla \cdot \left( \frac{\rho_a k_{r,a}}{\mu_a} \mathbf{K} \cdot (\nabla p_a - \rho_a \mathbf{g}) \right). \quad (2)$$

Here, the subscript  $a$  means that a property is evaluated for phase  $a$ ,  $\phi$  is the porosity,  $S_a$  is the saturation,  $k_{r,a}$  is the relative permeability,  $\mu_a$  is the viscosity,  $\mathbf{K}$  is the intrinsic permeability tensor (isotropic here,  $\mathbf{K} = K\mathbf{I}$ ),  $p_a$  is the pressure, and  $\mathbf{g}$  is the gravitational vector. This equation is solved twice; once for the wetting phase ( $a = w$ ), which represents the electrolyte, and once for the non-wetting phase ( $a = n$ ), which represents the gas phase.

In (2), there are two equations, but four unknowns ( $S_w$ ,  $S_n$ ,  $p_w$ , and  $p_n$ ). The saturations are related by a summation rule,  $S_n = 1 - S_w$ , leaving three unknowns. The wetting and non-wetting pressures are related by  $p_n = p_w + p_c$ , where  $p_c$  is the capillary pressure, which represents the pressure jump across a fluid-gas interface within the pore space. This capillary pressure is typically captured using an empirical model. In this case, we employ the popular van Genuchten formulation [5], which provides functional forms for  $p_c = f(S_w, S_n)$  and  $k_{r,a} = f(S_w, S_n)$ . These closure equations reduce the number

of unknowns to two, consistent with the two equations we will solve.

Typically, porous flow codes solve for  $p_n$  and  $S_w$  as their degrees of freedom, using the closure equations to calculate  $p_w$  and  $S_n$ . However, this poses a challenge for simulations with sharp changes in the material properties as in a battery, where the porosity and permeability differ between the anode, separator, and cathode. This causes a discontinuity in the saturation across an interface between two layers, which is difficult to capture using a continuous finite element formulation. To overcome this obstacle, we modified our code to solve for  $p_n$  and  $p_w$ , which are both continuous across material boundaries. This modification enables the stable solution of two-phase porous flow in a battery cell.

*Solid mechanics:* Deformation of the pellets is captured using a standard quasi-static conservation equation,

$$\nabla \cdot \mathbf{T} = 0, \quad (3)$$

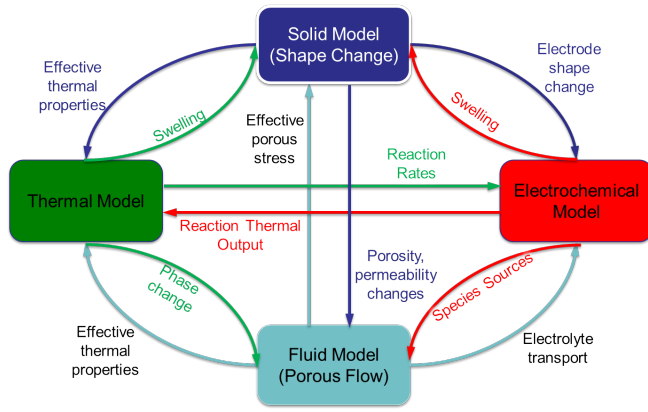
where  $\mathbf{T}$  is the solid stress tensor. For all materials except the separator, a simple linear elastic constitutive model for the stress is used,  $\mathbf{T} = \lambda \text{tr}(\mathbf{E})\mathbf{I} + 2G\mathbf{E}$ , where  $\mathbf{E} = \frac{1}{2}(\nabla \mathbf{d} + \nabla \mathbf{d}^T)$ ,  $\lambda$  and  $G$  are the moduli of the composite separator, and  $\mathbf{d}$  is the displacement vector.

To capture the large deformation of the separator upon melting, we have developed a phenomenological constitutive model that takes into account the load state during the melting transformation to create the volumetric and axial strains that are observed with experiments. In this model, we multiplicatively decompose the deformation gradient associated with the cold state combined material and hot state solid skeleton into three components associated with different phenomena:

- $\mathbf{F}^\Theta$ , volumetric deformation due to thermal expansion of each phase, the specific volume changes associated with melting of the electrolyte, the loss of void (air) space, and transport of the electrolyte phase
- $\mathbf{F}^X$ , permanent shape and volume change of the solid skeleton during the cold-to-hot phase transition
- $\mathbf{F}^M$ , elastic deformation experienced by the cold state solid and hot state solid skeleton

Various rules for flow, deformation, and phase change are used to calculate these decomposed quantities, but this model is too complicated to discuss here. Instead, we refer to the reader to a detailed report that is currently in preparation [6].

*Multiphysics coupling:* The critical path towards a useful performance model is coupling the various physics described previously into a single simulation. A key challenge in this path is determining which models need to be coupled to accurately capture the physics, and how those models are going to be coupled, i.e. what variables will be shared between the models and how they will be included in the appropriate constitutive equations. While ideally one may wish to fully-couple all of



**Figure 3.** Representation of the various physics models and potential couplings between each of them. The colored text and arrows represent information belonging to a certain set of physics (of the same color) being transferred to another set of physics.

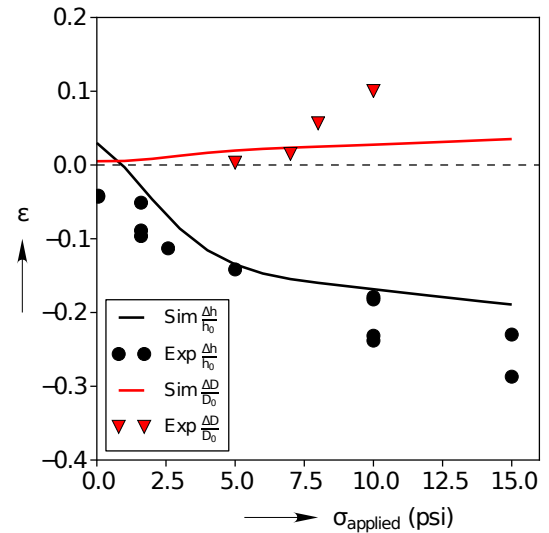
the physics, this is often not computationally practical. Figure 3 shows how physical phenomena from one model may potentially influence the behavior of the other models. Each additional coupling increases the complexity of the governing equations, thereby increasing the nonlinearity of the problem and drastically increasing solve times. Therefore, care must be taken to only couple physics where necessary.

In addition to correctly choosing which models are coupled, there are options on how tightly coupled the models are in the computational framework. If the relevant physical timescales are on the same order of magnitude and the coupling between the physics are strong, then the equations should be solved simultaneously in the same equation system. This is likely the case for the electrolyte transport and solid mechanics; deformation of the solid will immediately lead to a large change in the pressure and flow of the electrolyte. Alternatively, if the relevant time scales are disparate and the coupling is more weak, then the equations can be solved in a segregated fashion, where at any given time the degrees of freedom from one model can be considered fixed to the other model allowing solution in separate linear systems. This is most likely the case for the thermal and solid models, where the thermal transport is not strongly influenced by small deformations in the solid.

The segregated framework is highly preferred, as it drastically improves model performance, at the risk of lower stability and additional errors. However, Sierra/Aria allows for easy exploration of the effects of coupling, and when the models are fully integrated, various coupling schemes will be evaluated. Our expected outcome is that the solid and fluid mechanics will be solved simultaneously, while the thermal transport and electrochemistry will be segregated.

## Results and Discussion

In this section, we demonstrate simulations of two separate physics models. First we show the results of preliminary validation simulations for the custom constitutive model for solid

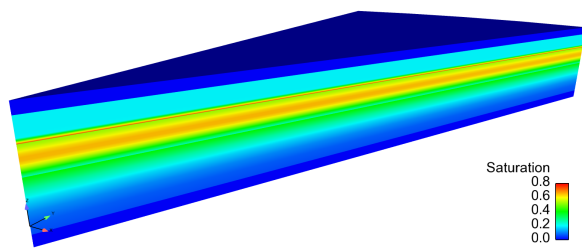


**Figure 4.** Fit and predicted axial and diameter strains under bonded boundary conditions. Experimental data courtesy of C. C. Roberts.

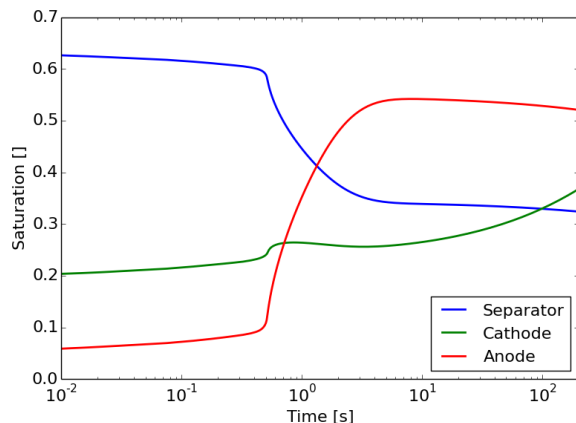
mechanics. Second, we test the two-pressure formulation for porous flow on a model battery cell.

*Constitutive model for solid mechanics:* In an effort to validate the solid mechanics constitutive model, our collaborators have performed a number of experiments quantifying the axial and transverse strains under a number of different axial stress conditions. In these experiments, a separator was placed between two platens and a constant axial force was applied. The system was then heated to above the melting point of the electrolyte, and the strains were measured [6]. The solid mechanics model for the separator was also run under similar conditions, with the assumption that the separator was bonded to the platens, which is similar to the observed conditions. The unknown material properties in the constitutive equations were then fit (calibrated) to the experimental data, and the results of this calibration are shown in Figure 4.

The model results in Figure 4 show reasonable agreement with the experimental data, particularly in the axial strain results. The simulation results show two regimes of behavior, one for pressures  $< 5$  psi and one for pressures  $> 5$  psi. It is arguable if the experimental data shows these two regimes distinctly. Conversely, the diameter strain experimental data clearly shows two regimes, with no strain at lower pressures and significant strain at higher pressures. This behavior is consistent with our mechanistic understanding that during the early stages of compression, the separator is simply losing “void”, or gas, space, causing the material to respond with an effective Poisson’s ratio of near zero. However, once all of the void space is removed, the material is a fully saturated solid, acting like an incompressible liquid, and responds with a Poisson’s ratio near 0.5. Unfortunately, the current constitutive model is unable to capture these two regimes. This is an area for future improvement of the model.



**Figure 5.** Snapshot of a simulation of two-phase porous flow with static geometry. Colors shown are the electrolyte saturation in each layer.



**Figure 6.** Volume average saturation for individual material layers throughout time. The abrupt change at  $\sim 0.5$  s is correlated to the point in time that the electrolyte in the separator begins to melt.

*Two-phase flow of electrolyte:* The new two-pressure formulation for porous flow was tested in the single cell geometry shown in Figure 2. Each material was initialized with a porosity and saturation consistent with the real materials. In order to model the melting of the solid electrolyte, the viscosity of the electrolyte was artificially increased by three orders of magnitude to prevent flow prior to melting. The porous flow was coupled to the thermal model, including an advancing burn front in the heat pellet.

The results of this simulation are shown in Figures 5 and 6. Figure 5 shows the saturation state throughout the stack just after melting. You can see the sharp jump in saturation that appears between the separator and the cathode, which would not have been possible with the standard pressure-saturation formulation. In Figure 6, The volume average saturation for each of the active layers is shown as a function of time. Here, the melting transition can be clearly seen at  $\sim 0.5$  s, followed by rapid wicking into the relatively dry anode and then a slower transport process into the cathode, all the while depleting the electrolyte in the separator.

In this simulation, the separator is depleted of electrolyte because it is not allowed to compress, as it does in reality. This

is because we have not coupled the fluid flow to the solid mechanics in this simulation. When the separator compresses, void space is removed, leading to an increase in the saturation. This will be improved in future simulations that will couple the thermal, fluid, and solid transport.

## Conclusions

In this paper, we presented a concept for a multiphysics model of molten salt battery performance that includes thermal, solid, and fluid transport coupled to electrochemistry. Models for the relevant physics were shown, and we discussed the impact of coupling physics and the different solution strategies. Finally, we demonstrated both the solid and fluid models, discussing areas of future coupling and improvement.

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